

I, the undersigned, who have prepared English translation which is attached herewith, hereby declare that the aforementioned translation is true and correct translation of officially certified copy of the Korean Patent Application No. 2003-35345 filed on June 2, 2003.

January 16, 2007

Translator : Suk-Cheol Yang
Suk-Cheol YANG

[Abstract of the Disclosure]

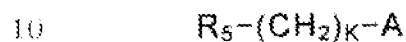
[Abstract]

5 A cleaning solution having a corrosion inhibitor of the formula 1 and a surfactant of the formula 2 is disclosed.

<Formula 1>



<Formula 2>



In the formula 1, any one of R_1 and R_4 is the hydroxyl group (-OH) and the other is hydrogen (-H), a halogen element (-X) or one functional group selected from the group consisting of alkyl (-R) group, alkoxy (RO-) group, amino (-NH₂) group, nitro (-NO₂) group, mercapto (-SH) group, 15 hydroxyl (-OH) group, aldehyde (-CHO) group and carboxyl (-COOH) group. R_2 and R_3 are hydrocarbons having 0~10 carbons and straight or branched structure. In the formula 2, R_5 is methyl group and K is an integer ranging from 3 to 22. A is HO(CH₂CH₂O)_L(CH(CH₃)CH₂O)_M⁻ or hydroxyl group. At this time, L and M are integers ranging from 0 to 15.

20 [Key Words]

corrosion inhibitor, triple bond, hydroxy group

[Specification]

[Title of the Invention]

**CLEANING AGENT WITH A CORROSION INHIBITOR IN A
PROCESS OF FORMING A SEMICONDUCTOR DEVICE**

[Detailed Description of the Invention]

[Object of the Invention]

[Field of the Invention and Prior Art related to the Invention]

The present invention relates to a cleaning solution used in a process of fabricating a semiconductor device, and more particularly to a cleaning solution with a corrosion inhibitor.

In a semiconductor device, a metal such as aluminum, copper or tungsten is frequently used for an interconnect or a contact plug. Recently, as a semiconductor device becomes highly integrated, a gate electrode is formed of a metal for reducing resistance of the gate electrode. In order to form the gate electrode or the interconnect, a metal layer should be deposited and patterned. Then a cleaning process is performed for removing byproducts such as polymer that may occur after the patterning process. At this time, the cleaning process usually employs a conventional cleaning solution such as a standard cleaning 1 (SC1) or a sulfuric peroxide mixture (SPM). The SC1 is a mixed solution of ammonia water (NH_4OH), hydrogen peroxide (H_2O_2) and deionized water (H_2O), and the SPM is a mixed solution of sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2). However, the strong oxidizing agent such as the hydrogen peroxide

severely corrodes metals such as tungsten during the cleaning process.

Therefore, a corrosion inhibitor is used for preventing the corrosion of the metal. Conventional corrosion inhibitors employ material of aromatic hydrocarbons such as benzotriazole and 5-methylbenzoimidazole. However, the material of aromatic hydrocarbons cause environmental problems and are harmful to human health. The United Patent Application No. 6,200,947 discloses materials such as 2-mercaptoethanol and thioglycerol which are aromatic alcohols having a mercapto group as corrosion inhibitors. These materials are environmentally sound. However, the corrosion inhibitors of aromatic alcohols having a mercapto group severely etch polysilicon to form an undercut region at a polysilicon pattern or to form a pit at a silicon substrate.

[Technical Object of the Invention]

It is therefore an aspect of embodiments of the invention to provide a environmentally sound cleaning solution capable of preventing corrosion of metals and reducing etched amount of polysilicon.

[Construction of the Invention]

Embodiments of the invention are directed to a cleaning solution having a corrosion inhibitor having a triple bond and at least one hydroxyl group (-OH).

The corrosion inhibitor has the below formula 1.

<Formula 1>



In the formula 1, any one of R_1 and R_4 is the hydroxyl group (-OH) and the other is hydrogen (-H), a halogen element (-X) or one functional group selected from the group consisting of alkyl (-R) group, alkoxy (RO-) group, amino (-NH₂) group, nitro (-NO₂) group, mercapto (-SH) group, hydroxyl (-OH) group, aldehyde (-CHO) group and carboxyl (-COOH) group. R_2 and R_3 are hydrocarbons having 0~10 carbons and straight or branched structure.

More particularly, the other of R_1 and R_4 may be methyl group (-CH₃) or methoxy group (-OCH₃).

The corrosion inhibitor of the formula 1 may be included into the cleaning solution with about 0.0001~10 wt.% of the cleaning solution. More preferably, the corrosion inhibitor may be included with about 0.001~1wt.% thereof.

2-Butyne-1,4-diol may be a representative as the corrosion inhibitor of the formula 1. At this time, R_1 and R_4 are hydroxyl group and R_2 and R_3 are -CH₂-.

The corrosion inhibitor has a linear structure to be naturally decomposed and environmentally sound. Additionally, the triple bond of the corrosion inhibitor can prevent corrosion of metals. This may be because the metal doesn't lose electrons due to the lots of electrons existing in the triple bond. The corrosion inhibitor may be easily dissolved in water due to the hydroxyl group contained therein. Also, the corrosion inhibitor may function as a surfactant at an interface between a metal and the cleaning solution or between polysilicon and the cleaning solution due to the hydroxyl group contained therein. The corrosion inhibitor reduces damage

of the polysilicon. This is because the corrosion inhibitor is absorbed on a surface of the polysilicon and protects the surface of the polysilicon. R_1 and R_4 may be controlled to increase solubility in water and surface-active ability at the interface between the cleaning solution and the polysilicon.

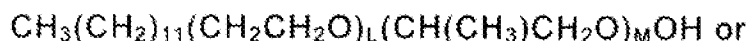
5 The cleaning solution may further include a surfactant having the below formula 2.

<Formula 2>



In the formula 2, R_5 is methyl group and K is an integer ranging from
10 3 to 22. A is $HO(CH_2CH_2O)_L(CH(CH_3)CH_2O)_M-$ or hydroxyl group. At this time, L and M are integers ranging from 0 to 15. The surfactant may be included into the cleaning solution with about 0.0001~10wt. % of the cleaning solution. More preferably, the surfactant may be included with about 0.001~1wt. % thereof.

15 $C_{12}H_{25}O(CH_2CH_2O)_JH$ may be a representative of the surfactant of the formula 2. At this time, J is an integer ranging from 5 to 15. When R_5 is methyl group and K is 11, and when L is equal to J and M is zero in the formula 2, $C_{12}H_{25}O(CH_2CH_2O)_JH$ may be obtained.



20 $CH_3(CH_2)_{17}(CH_2CH_2O)_L(CH(CH_3)CH_2O)_MOH$ may be another representative of the surfactant of the formula 2.

$CH_3(CH_2)_{11}(CH_2CH_2O)_L(CH(CH_3)CH_2O)_MOH$ is an adduct of propylene oxide and ethylene oxide of lauryl alcohol, and

$CH_3(CH_2)_{17}(CH_2CH_2O)_L(CH(CH_3)CH_2O)_MOH$ is an adduct of propylene oxide
25 and ethylene oxide of stearyl alcohol.

The surfactant may be synthesized by being extracted from a coconut or a palm tree and has a linear structure to be naturally decomposed and environmentally sound. The surfactant reduces damage of polysilicon and protects the surface of the polysilicon by being absorbed thereon. Also, the surfactant may function of cleaning particles on the polysilicon or on metals. Ratio of K, L and M may be changed to control solubility in water and surface-active ability at the interface between the polysilicon and the cleaning solution.

The cleaning solution may further include an acid solution or an alkaline solution. The alkaline solution may be selected from the group consisting of sodium hydroxide (NaOH), potassium hydroxide (KOH), ammonium hydroxide (NH₄OH), tetramethyl ammonium hydroxide (N(CH₃)₄OH) and chloride solution. The alkaline solution may be included with 0.0001~10 wt.% of the cleaning solution and more preferably with 0.01~5wt.% thereof. To use a cleaning solution including the alkaline solution is preferable in a cleaning solution after a copper damascene process or a planarization process such as a chemically mechanically polishing (CMP).

The acid solution may be selected from the group consisting of hydrochloric acid (HCl), nitric acid (HNO₃), sulfuric acid (H₂SO₄), phosphoric acid (mP₂O₅·nH₂O), fluoric acid (HF) and an organic acid. The organic acid may be selected from the group consisting of citric acid, tricarballic acid, tartaric acid, succinic acid, malic acid, aspartic acid, glutaric acid, adipic acid, suberic acid, oxalic acid, acetic acid and fumaric acid. The acid solution may be included with 0.0001~10wt.% of the cleaning

solution and more preferably with 0.01~5 wt.% thereof.

The present invention will now be described more fully hereinafter. This invention may, however, be embodied in many different forms and should not be construed as limited to the embodiments set forth herein.

5 Rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the invention to those skilled in the art.

<Experiment 1: A test for the cleaning solution including the corrosion inhibitor of the formula 1>

10 Experiment 1 was performed under conditions of table 1 in order to investigate effects of the corrosion inhibitor of the formula 1. In the present experiment, three cleaning solutions were prepared. Cleaning solution 1 was prepared with 200ml of deionized water and 20ml of 3% ammonia solution but without any corrosion inhibitor. Cleaning solution 2 was
15 prepared with 200ml of deionized water, 20ml of 3% ammonia solution and 0.2g of 2-mercaptoethanol which is a conventional corrosion inhibitor. Cleaning solution 3 was prepared with 200ml of deionized water, 20ml of 3% ammonia solution and 0.2g of 2-butyne 1,4-diol. After preparing three cleaning solutions, three tungsten blanket wafers and three polysilicon
20 blanket wafers were prepared. A thermal oxide layer was formed on a silicon bare wafer with a thickness of 1000Å and a tungsten layer was formed on the thermal oxide layer with a thickness of 500Å, thereby preparing the tungsten blanket wafer. A thermal oxide layer was formed on a silicon bare wafer with a thickness of 1000Å and a polysilicon layer was
25 formed on the thermal oxide layer with a thickness of 850Å, thereby

preparing the polysilicon blanket wafer. Each of the tungsten blanket wafer and the polysilicon blanket wafer was treated during 10 minutes at a temperature of 65°C by using the cleaning solutions 1, 2 and 3, and the result was reported in the below table 1.

Table 1

	Cleaning solution 1	Cleaning solution 2	Cleaning solution 3
3% Ammonia solution	20ml	20ml	20ml
2-Mercaptoethanol	-	0.2g	-
2-Butyne 1,4-diol	-	-	0.2g
Deionized water	200ml	200ml	200ml
Uniformity of tungsten	Bad	Good	Good
Etched amount of polysilicon(Å)	93~850	480~850	168~224
Uniformity of polysilicon	Bad	Bad	Good

Referring to table 1, when the cleaning solution 1 without a corrosion inhibitor was used, uniformity of tungsten is bad. When the cleaning solution 2 having the conventional corrosion inhibitor was used, the tungsten layer was not corroded to represent good uniformity of the tungsten layer, but much amount of the polysilicon was etched to be improper. However, when the cleaning solution 3 having the corrosion inhibitor according to the present invention was used, both uniformities of the polysilicon and the tungsten were good and only little amount of the polysilicon was etched. Therefore, the cleaning solution 3 was proper for a

reliable cleaning process.

<Experiment 2: A test for the cleaning solution including the corrosion inhibitor of the formula 1 and the surfactant of the formula 2>

Two identical tungsten blanket wafers and two identical polysilicon blanket wafer were prepared. The tungsten blanket wafer and the polysilicon blanket wafer were made by using the same method with the experiment 1. 220 μ l of $C_{12}H_{25}O(CH_2CH_2O)_jH$, which is a kind of the surfactant of the formula 2, was added into the cleaning solution 3 of the experiment 1 to prepare a cleaning solution 4. 220 μ l of $C_{12}H_{25}O(CH_2CH_2O)_jH$ was added into the cleaning solution 2 having the conventional corrosion inhibitor of the experiment 1 to prepare a cleaning solution 5. Each of the tungsten blanket wafer and the polysilicon blanket wafer was treated during 30 minutes at a temperature of 65°C by using the cleaning solutions 4 and 5. This result was reported in the below table 2.

Table 2

	Cleaning solution 4	Cleaning solution 5
3% Ammonia solution	20ml	20ml
2-Mercaptoethanol	-	0.2g
2-Butyne 1,4-diol	0.2g	-
Deionized water	200ml	200ml
$C_{12}H_{25}O(CH_2CH_2O)_jH$	220 μ l	220 μ l
Uniformity of tungsten	Good	Good
Etched amount of polysilicon(Å)	38	75.2
Uniformity of polysilicon	Good	Good

Referring to table 2, using both of the cleaning solutions 4 and 5 made both of good uniformities of the tungsten and the polysilicon. But, the etched amount of the polysilicon was less in a case of using the cleaning solution 4 in comparison with another case of using the cleaning solution 5.

Therefore, through the experiments 1 and 2, the cleaning solution including the corrosion inhibitor of the formula 1 and the surfactant of the formula 2 according to the present invention indicated the best result.

Although the experiments 1 and 2 employed tungsten blanket wafer, it will be apparent to those skilled in the art that the cleaning solution of the present invention can be applied to any metal such as copper, aluminum, titanium, tantalum, iridium, cobalt and etc or nitride of the metal.

[Effect of the Invention]

Accordingly, the cleaning solution having the corrosion inhibitor according to the present invention is environmental-friendly and capable of preventing the corrosion of metal and reducing damage of polysilicon.

[Scope of Claim]

[Claim 1]

5 A cleaning solution comprising deionized water, a surfactant and a corrosion inhibitor comprising triple bond and at least one hydroxyl group.

[Claim 2]

The cleaning solution as claimed in Claim 1, wherein the corrosion
10 inhibitor has the below formula 1,

<Formula 1>



wherein any one of R_1 and R_4 is the hydroxyl group (-OH) and the other is hydrogen (-H), a halogen element (-X) or one functional group
15 selected from the group consisting of alkyl (-R) group, alkoxy (RO-) group, amino (-NH₂) group, nitro (-NO₂) group, mercapto (-SH) group, hydroxyl (-OH) group, aldehyde (-CHO) group and carboxyl (-COOH) group; and

R_2 and R_3 are hydrocarbons having 0~10 carbons and straight or branched structure.

20

[Claim 3]

The cleaning solution as claimed in Claim 2, wherein the other of R_1 and R_4 is methyl group (-CH₃) or methoxy group (-OCH₃).

25 [Claim 4]

The cleaning solution as claimed in Claim 2, the corrosion inhibitor of the formula 1 is included into the cleaning solution with about 0.0001~10 wt.% of the cleaning solution.

5 [Claim 5]

The cleaning solution as claimed in Claim 1, the corrosion inhibitor is 2-butyne-1,4-diol.

[Claim 6]

10 The cleaning solution as claimed in Claim 1, wherein the surfactant has the below formula 2,

<Formula 2>



wherein R_5 is methyl group;

15 K is an integer ranging from 3 to 22; and

A is $HO(CH_2CH_2O)_L(CH(CH_3)CH_2O)_M-$ or hydroxyl group, wherein L and M are integers ranging from 0 to 15.

[Claim 7]

20 The cleaning solution as claimed in Claim 6, wherein the surfactant is included into the cleaning solution with about 0.0001~10wt.% of the cleaning solution.

[Claim 8]

25 The cleaning solution as claimed in Claim 1, wherein the surfactant

is $C_{12}H_{25}O(CH_2CH_2O)_JH$, wherein J is an integer ranging from 5 to 15.

[Claim 9]

The cleaning solution as claimed in Claim 1, further comprising an
5 acid solution or an alkaline solution.

[Claim 10]

The cleaning solution as claimed in Claim 9, wherein the alkaline
solution is at least one solution selected from the group consisting of
10 sodium hydroxide (NaOH), potassium hydroxide (KOH), ammonium
hydroxide (NH₄OH), tetramethyl ammonium hydroxide (N(CH₃)₄OH) and
chloride solution.

[Claim 11]

15 The cleaning solution as claimed in Claim 9, wherein the alkaline
solution is included with 0.0001~10 wt.% of the cleaning solution.

[Claim 12]

The cleaning solution as claimed in Claim 9, wherein the acid
20 solution is at least one solution selected from the group consisting of
hydrochloric acid (HCl), nitric acid (HNO₃), sulfuric acid (H₂SO₄),
phosphoric acid (mP₂O₅·nH₂O), fluoric acid (HF) and an organic acid.

[Claim 13]

25 The cleaning solution as claimed in Claim 12, wherein the organic

acid is selected from the group consisting of citric acid, tricarballic acid, tartaric acid, succinic acid, malic acid, aspartic acid, glutaric acid, adipic acid, suberic acid, oxalic acid, acetic acid and fumaric acid.

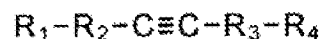
6 [Claim 14]

The cleaning solution as claimed in Claim 9, wherein the acid solution is included with 0.0001~10 wt.% of the cleaning solution.

[Claim 15]

10 A cleaning solution comprising a corrosion inhibitor having the below formula 1,

<Formula 1>



wherein any one of R_1 and R_4 is the hydroxyl group (-OH) and the
15 other is hydrogen (-H), a halogen element (-X) or one functional group selected from the group consisting of alkyl (-R) group, alkoxy (RO-) group, amino (-NH₂) group, nitro (-NO₂) group, mercapto (-SH) group, hydroxyl (-OH) group, aldehyde (-CHO) group and carboxyl (-COOH) group; and

R_2 and R_3 are hydrocarbons having 0~10 carbons and straight or
20 branched structure.

[Claim 16]

The cleaning solution as claimed in Claim 15, wherein the other of R_1 and R_4 is methyl group (-CH₃) or methoxy group (-OCH₃).

[Claim 17]

The cleaning solution as claimed in Claim 15, the corrosion inhibitor of the formula 1 is included into the cleaning solution with about 0.0001~10 wt.% of the cleaning solution.

[Claim 18]

The cleaning solution as claimed in Claim 15, the corrosion inhibitor is 2-butyne-1,4-diol.

[Claim 19]

The cleaning solution as claimed in Claim 15, further comprising a surfactant having the below formula 2,

<Formula 2>



wherein R_5 is methyl group;

K is an integer ranging from 3 to 22; and

A is $HO(CH_2CH_2O)_L(CH(CH_3)CH_2O)_M-$ or hydroxyl group, wherein L and M are integers ranging from 0 to 15.

[Claim 20]

The cleaning solution as claimed in Claim 19, wherein the surfactant is included into the cleaning solution with about 0.0001~10wt.% of the cleaning solution.

[Claim 21]

The cleaning solution as claimed in Claim 19, wherein the surfactant is $C_{12}H_{25}O(CH_2CH_2O)_JH$, wherein J is an integer ranging from 5 to 15.

[Claim 22]

5 The cleaning solution as claimed in Claim 15, further comprising an acid solution or an alkaline solution.

[Claim 23]

10 The cleaning solution as claimed in Claim 22, wherein the alkaline solution is at least one solution selected from the group consisting of sodium hydroxide (NaOH), potassium hydroxide (KOH), ammonium hydroxide (NH_4OH), tetramethyl ammonium hydroxide ($N(CH_3)_4OH$) and chloride solution.

15 [Claim 24]

The cleaning solution as claimed in Claim 22, wherein the alkaline solution is included with 0.0001~10 wt.% of the cleaning solution.

[Claim 25]

20 The cleaning solution as claimed in Claim 22, wherein the acid solution is at least one solution selected from the group consisting of hydrochloric acid (HCl), nitric acid (HNO_3), sulfuric acid (H_2SO_4), phosphoric acid ($mP_2O_5 \cdot nH_2O$), fluoric acid (HF) and an organic acid.

25 [Claim 26]

The cleaning solution as claimed in Claim 25, wherein the organic acid is selected from the group consisting of citric acid, tricarballic acid, tartaric acid, succinic acid, malic acid, aspartic acid, glutaric acid, adipic acid, suberic acid, oxalic acid, acetic acid and fumaric acid.

6

[Claim 27]

The cleaning solution as claimed in Claim 22, wherein the acid solution is included with 0.0001~10 wt.% of the cleaning solution.